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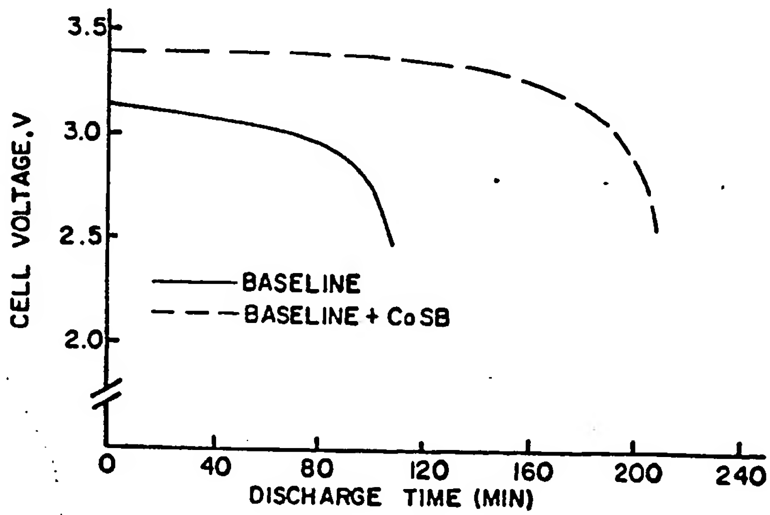
(54) Title: HIGH RATE METAL OXYHALIDE CELLS



$Li/SOCl_2$ 3-PLATE LAB CELLS W/0.5mm CATHODES, CONSTANT CURRENT DENSITY OF 9mA/cm^2. 1.5 M $LiAlCl_4/SOCl_2$, 4.5° C

(57) Abstract

Improved catalysts for the reduction of oxyhalide depolarizers such as $SOCl_2$ and SO_2Cl_2 in active-metal non-aqueous cells are provided which are easier to prepare and less expensive than phthalocyanine complexes and which are generally more stable in the cell environment. These catalysts include certain macrocyclic complexes of Schiff's base prepared by the reaction of an aldehyde with a primary diamine. The preferred embodiments include mononuclear metal macrocyclic complexes made from salicylaldehyde and o-phenylenediamine and binuclear metal macrocyclic complexes of 5-methyl isophthalaldehyde and 1,3-diaminopropane.

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HIGH RATE METAL OXYHALIDE CELLS

BACKGROUND OF THE INVENTION

The invention herein described was made in the source of or under a contract or subcontract thereunder with the Department of the Army.

Field of the Invention

The present invention relates generally to the field of non-aqueous electrochemical cells and, more particularly to a class of catalysts for the reduction of oxyhalide depolarizers such as $SOCl_2$ and SO_2Cl_2 in such cells.

Description of the Prior Art

Much work has been done in the field of high energy battery systems utilizing highly reactive anode materials such as alkali or alkaline earth metals in combination with a non-aqueous electrolyte. The electrolyte is normally composed of a solute which is commonly a metal salt or a complex metal salt of the anode metal dissolved in a compatible non-aqueous solvent

depolarizer such as SO_2, $SOCl_2$, or SO_2Cl_2. An inert cathode, usually of carbon black, is also used in such cells.

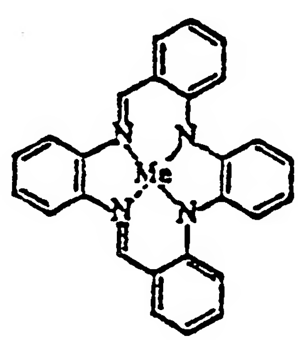
The potential of electrochemical couples, such as those mentioned above as high rate, high-power batteries, has not been fully realized mainly because of excessive cathode polarization particularly at high discharge rates and low operating temperatures. This causes a deterioration of cell performance after a short period of operation. For this reason, much research has been conducted concerning the development of additives such as catalysts to reduce the cathode depolarizer, thereby improving the rate capability of the cathodes.

Some improvement in the rate capability of these carbon cathodes has been achieved by doping them with metals such as platinum or metal halides. However, high amounts of the metals or metal halides are required to effectively increase the rate capability of cells such as $Li/SOCl_2$ cells. Also, the cell performance of these dopants deteriorates with thinner electrodes and at the higher temperatures required for certain applications. More recently, metal-phthalocyanine complexes have been shown to possess significant catalytic activity for the electrochemical reduction of solvent depolarizers such as

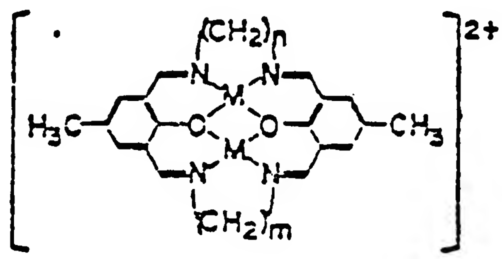
thionyl chloride or sulfural chloride, thereby increasing cell capacity. Examples of such are found in U.S. patents 4,252,875 and 4,405,693. The need still exists for the provision of catalyzed cathodes for cells such as $Li/SOCl_2$ cells which are stable and effective over a wide temperature range and which are sufficiently stable in the cell to be used in both active and reserve configurations.

SUMMARY OF THE INVENTION

By means of the present invention, improved catalysts for the reduction of oxyhalide depolarizers such as $SOCl_2$ and SO_2Cl_2 are provided which are easier to prepare and less expensive than phthalocyanine complexes and which are generally more stable in the cell environment. These catalysts include certain macrocyclic complexes of Schiff's base prepared by the reaction of an aldehyde with a primary diamine. The preferred embodiments include mononuclear metal macrocyclic complexes made from salicylaldehyde and o-phenylenediamine of a structure such as



and binuclear metal macrocyclic complexes of 5-methyl isophthalaldehyde and 1,3-diaminopropane having a structure such as



where M or Me represents a metal selected from the group consisting of iron and cobalt and m and n represent integers.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIGURE 1 is a graphical representation of the discharge characteristics of a $Li/SOCl_2$ cell employing prior art catalysts cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc) dissolved in the electrolyte compared with the uncatalyzed baseline.

FIGURE 2 is a graphical representation showing the discharge characteristics of a $Li/SOCl_2$ cell using mononuclear CoSB catalyst compared with the uncatalyzed baseline.

FIGURE 3 is a graphical representation of polarization characteristics of a Li/$SOCl_2$ cell using binuclear metal complexes FeMac and CoMac of the invention;

FIGURE 4 is a graphical representation of the discharge characteristics of a cell of FIGURE 2 at 23°C and 63°C with and without CoSB.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Catalyst Preparation

The syntheses of FeMac and CoMac were carried out using the method of Pilkington et al, Australian Journal of Chemistry Vol. 23, 2225 (1970). The syntheses of CoSB and FeSB were carried out using a method described in Jahnke et al, Topics in Current Chemistry, Vol. 1, 133 (1979).

Example 1

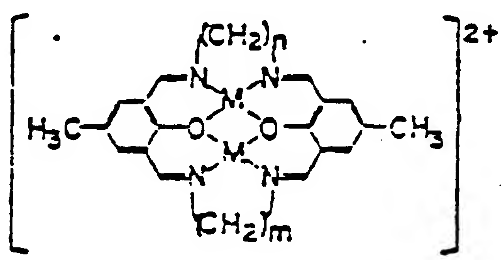
A solution of 5-methyl isophthalaldehyde (0.05 mole) dissolved in the minimum volume of boiling methanol was added to a suspension formed by mixing 1,3-diaminopropane (0.05M) with a saturated solution of cobalt chloride in methanol. The mixture was heated under reflux for 1 hour. Methanol was removed by boiling at

atmospheric pressure. The product was poured into ten times its volume of tetrahydrofuran. The product was filtered, washed with water and dried.

Example 2

The process of Example 1 was repeated except that iron chloride was substituted for cobalt chloride of Example 1.

The process of Examples 1 and 2 produced binuclear metal macrocyclic complexes CoMac and FeMac, repectively, of the following structure:



where M represents iron or cobalt and m and n are integers.

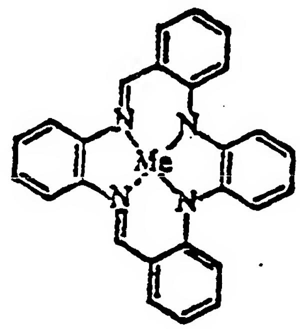
Example 3

A solution of salicylaldehyde (0.05M), o-phenylenediamine (0.05M) and cobalt acetate (0.025M) was refluxed in ethanol for about 30 minutes. The resulting product was washed with cold methanol and dried at 120°C.

Example 4

Example 3 was repeated substituting iron acetate for the cobalt acetate.

The structure of the complexes formed in Examples 3 and 4 known as CoSB and FeSB, respectively, was as follows:



Performance of Catalyst in Cells

Tables 1 and 2 show a comparison of discharge characteristics of cells using a prior art catalyst, the catalyst of Example 3, and no catalyst.

TABLE 1. DISCHARGE CHARACTERISTICS OF $Li/SOCl_2$ CELLS WITH VARIOUS CATALYSTS WITH A CONSTANT CURRENT DENSITY OF 30 MA/cm^2 AT 23°C

Catalyst	Cell Voltage (V)	Discharge Life (Minutes)
None	2.92	34
Iron Phthalocyanine (FePc)	3.30	52
Mononuclear Couples with Schiff's Base (CoSB)	3.30	70

- ELECTROLYTE = (0.5 M $LiAlCl_4$ + 1.0 M $AlCl_3$)/$SOCl_2$
- CATHODE THICKNESS = 1.0 millimeter

TABLE 2. DISCHARGE CHARACTERISTICS OF $Li/SOCl_2$ CELLS WITH AND WITHOUT COSB COMPLEX AT A CONSTANT CURRENT LOAD OF 10 MA/cm^2 AT DIFFERENT OPERATING TEMPERATURES

Catalyst	-32°C Voltage at 50% DOD (V)	-32°C DOD (min)	-18°C Voltage at 50% DOD (V)	-18°C DOD (min)	23°C Voltage at 50% DOD (V)	23°C DOD (min)	63°C Voltage at 50% DOD (V)	63°C DOD (min)
None	2.70	55	2.80	80	3.12	105	3.36	164
CoSB	2.72	60	2.94	90	3.39	182	3.44	193

FIGURE 1 shows the discharge characteristics of prior art cells using cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc) catalysts dissolved in the electrolyte. It should be noted that the FePc exhibits a somewhat higher catalytic activity. FIGURES 2-4 show data derived using the catalysts of the present invention.

In FIGURES 2-4, the discharge characteristics of $Li/SOCl_2$ cells catalyzed by various metal macrocyclic complexes are compared to an uncatalyzed cell. All catalyzed cells showed substantial improvement in both cell voltage and specific cathode capacity over the uncatalyzed cell. These complexes have shown as good or better catalytic activity for the reduction of $SOCl_2$ than the iron phthalocyanine catalyst. In the case of metal pthalocyanine catalysts, FePc showed the best

catalytic activity, whereas, cobalt tetraphenylporphyrin (CoTPP) and cobalt Schiff's base complexes (CoSB) possess superior catalytic activity for $SOCl_2$ reduction than the iron complexes of these macrocyclic rings. Electronic charge density on the central metal ion, extent of orbital overlapping backbonding and the nature of the specific interaction of the complex with the carbon surface, are some of the factors that can influence the catalytic activity of these complexes for the reduction of $SOCl_2$. In the case of the binuclear macrocyclic complexes the iron couples appear to be superior.

The operating temperature also appears to influence the catalytic activity as shown in Table 2. In general, the cell performance improved with catalyzed cells irrespective of operating temperatures and current densities. At low operation temperatures, however, the catalytic activity of cobalt Schiff's base complex is rather reduced but the significance of this behavior is not yet understood. However, one of the factors could be the specific interaction of the CoSB complex with carbon cathode surface. A better way of impregnating the complex onto carbon should show better results since the performance of cells with this catalyst is drastically improved at high operating temperatures. The catalyst stability is projected to be responsible for the superior performance at high operating temperatures.

CLAIMS

The embodiments of the invention in which an exclusive property or right is claimed are defined as follows:

1. In a non-aqueous electrochemical cell system having an active metal anode, a cathode and a non-aqueous electrolyte having an oxyhalide depolarizer, the improvement comprising:

a catalyst for the reduction of said oxyhalide depolarizer comprising a metal complex of Schiff's base, said Schiff's base being selected from the group consisting of macrocyclic complexes of 5-methyl isophthalaldehyde and a diamino alkane and complexes of salicylaldehyde and o-phenylenediamine, and wherein the metal in said metal complex is selected from the group consisting of iron and cobalt.

2. The cell of claim 1 wherein said metal is cobalt.

3. The cell of claim 1 wherein said metal is iron.

4. The cell of claim 1 wherein said Schiff's base is one made from salisaldehyde and o-phenylenediamine and said metal complex is mononuclear.

5. The cell of claim 3 wherein said metal is cobalt.

6. The cell of claim 3 wherein said metal is iron.

7. The cell of claim 1 wherein said Schiff's base is one made from 5-methyl isophthalaldehyde and 1,3-diaminopropane and wherein said metal complex is binuclear.

8. The cell of claim 5 wherein said metal is cobalt.

9. The cell of claim 5 wherein said metal is iron.

10. In a non-aqueous electrochemical cell having a lithium anode, a carbon cathode and a non-aqueous electrolyte comprising $LiAlCl_4$ salt in $SOCl_2$ depolarizer solvent the improvement comprising:

a catalyst for the reduction of said oxyhalide depolarizer comprising a metal complex of Schiff's base, said shift base being selected from the group consisting of macrocyclic complexes of 5-methyl

(Claim 10 continued)

isophthalaldehyde and a diamino alkane and complexes of salicylaldehyde and o-phenylenediamine, and wherein the metal in said metal complex is selected from the group consisting of iron and cobalt.

11. The cell of claim 10 wherein said metal is cobalt.

12. The cell of claim 10 wherein said metal is iron.

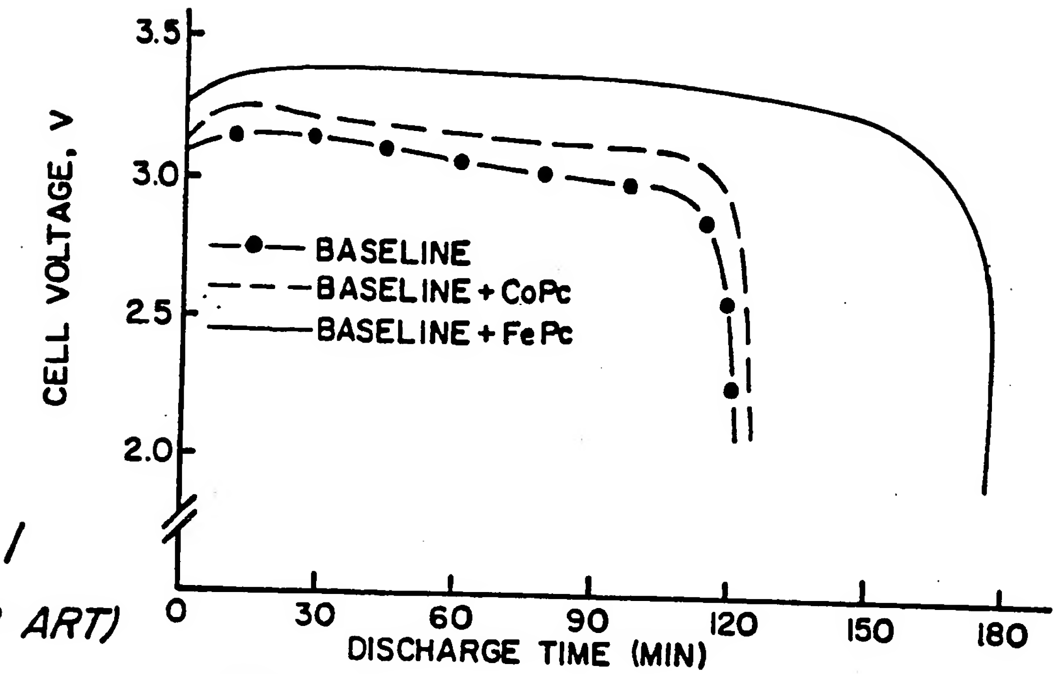


Fig. 1

(PRIOR ART)

$Li/SOCl_2$ CELLS W/0.5mm CATHODES, CONSTANT CURRENT DENSITY OF 10 mA/cm^2. 1.5 M $LiAlCl_4/SOCl_2$, 23° C.

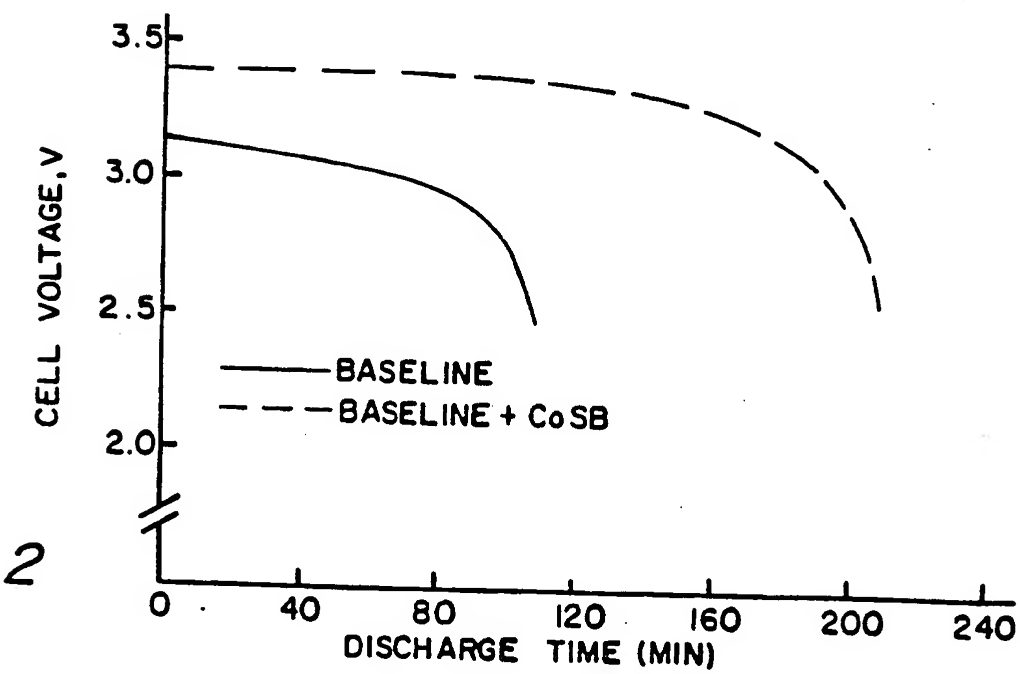


Fig. 2

$Li/SOCl_2$ 3-PLATE LAB CELLS W/0.5mm CATHODES, CONSTANT CURRENT DENSITY OF 9 mA/cm^2. 1.5 M $LiAlCl_4/SOCl_2$, 4.5° C.

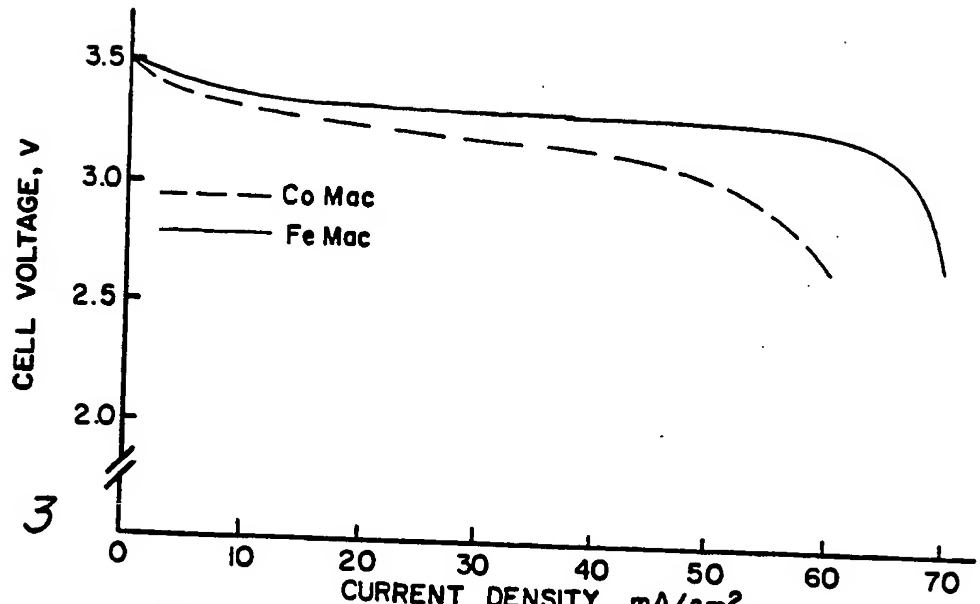


Fig. 3

Li/$SOCl_2$ LAB CELLS W/0.5 mm CATHODES.
1.5 M $LiAlCl_4$/$SOCl_2$, 23° C.

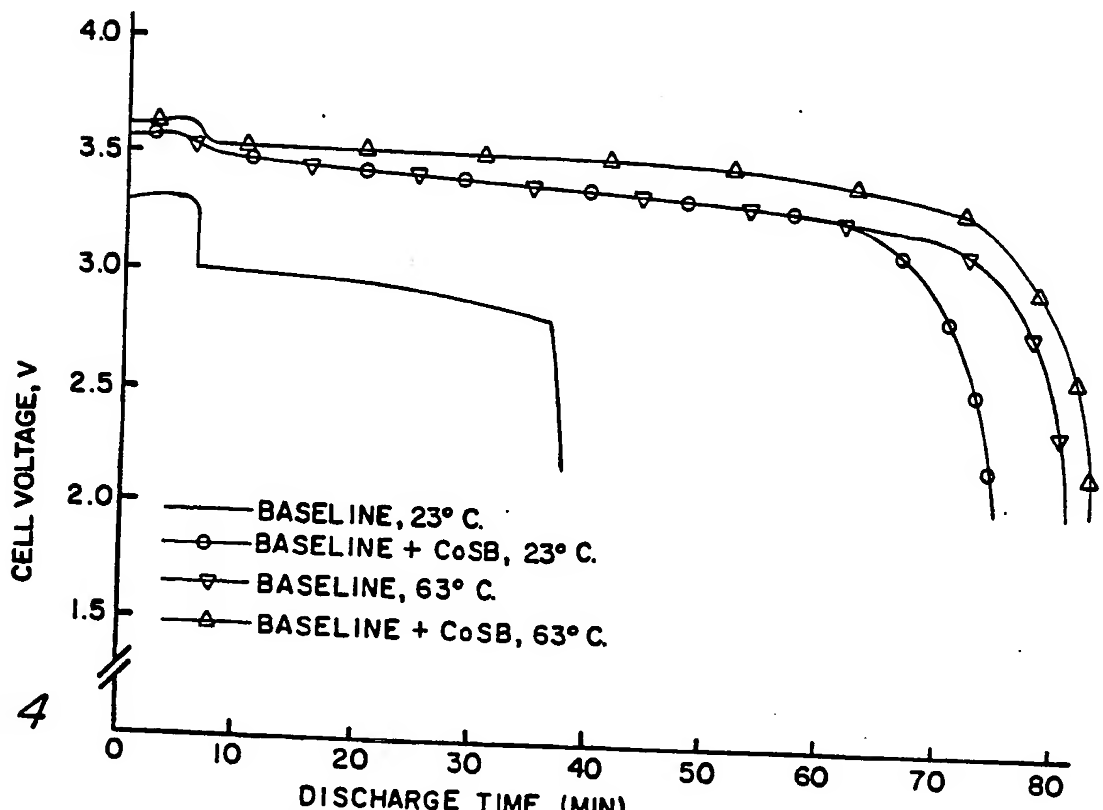


Fig. 4

Li/$SOCl_2$ CELLS WITH (1.0 M $AlCl_3$ + 0.5 M $LiAlCl_4$)/$SOCl_2$
AT 30 mA/cm².

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/01787

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: H 01 M 6/14; H 01 M 4/90

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	H 01 M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4469763 (F. WALSH et al.) 4 September 1984, see claim 1; column 4, lines 20-23 --	1
A	DE, A, 2052955 (BATTELLE INSTITUT) 4 May 1972	
A	Extended Abstracts, volume 83, no. 2, 9-14 October 1983, Washington, D.C., (US) F. Walsh et al.:"An improved Li/Soll$_2$ battery", abstract no. 33, see pages 54,55 --	
A	GB, A, 2108312 (HONEYWELL INC.) 11 May 1983, see claim 1	1

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* Special categories of cited documents: [10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
19th December 1985	30 JAN. 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 85/01787 (SA 10888)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 21/01/86

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4469763	04/09/84	EP-A- 0141209	15/05/85
DE-A- 2052955	04/05/72	None	
GB-A- 2108312	11/05/83	None	

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